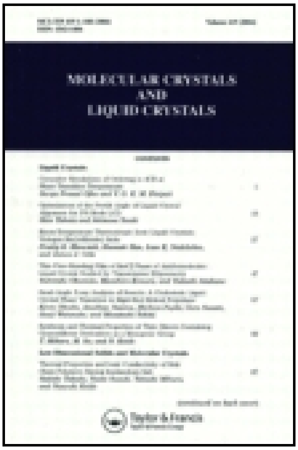

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Jacek Mayer [a], Maria Massalska-Arodz [a] & Jan Krawczyk [a]

[a] The Niewodniczański Institute of Nuclear Physics, 31-342 Krakíw, Radzikowskiego, 152, Poland

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Calorimetric and Dielectric Studies of Relaxation Accompanying a Glass Transition in the Right-Handed Isopentylcyanobiphenyl (5*CB)

JACEK MAYER, MARIA MASSALSKA-ARODŻ and
JAN KRAWCZYK

The Niewodniczański Institute of Nuclear Physics, 31–342 Kraków, Radzikowskiego 152, Poland

The specific heat measurements by means of the adiabatic calorimetry provided new information concerning the polymorphism of 5*CB. A relatively large enthalpy relaxation was observed in the vicinity of glass transition Temperature dependence of the relaxation time showed that the main contribution to the relaxation is due to the reorientations of 5*CB molecules around the short axes. The comparison of the calorimetric results with the dielectric relaxation times was performed. Data from both methods are well described by the Vogel-Fulcher-Tammann equation with the same fitting parameters.

Keywords: enthalpy relaxation; dielectric relaxation; glass; polymorphism

INTRODUCTION

Tendency of glass formation seems to be determined by two main factors, i.e. a large degree of disorder and a high packing coefficient $k = (V_o - V_f) / V_o$, where: V_o is the whole volume which is due to each molecule in a medium and V_f is the free volume in a medium available for molecule to move. Both factors help to avoid crystallization of the liquid sample. Transition from liquid (and/or liquid crystalline phase) to glass is a jamming process [1] driven by lowering the temperature when the magnitude of V_f decreases. Temperature T_g of glass transition is cooling rate dependent: a larger $\Delta T/\Delta t$ leads to a stronger decrease of V_f and consequently the transition to the glass takes place at higher T_g. In glass transition the ergodicity of the system is lost [2]. Diminishing of the $V_f(T)$ in the undercooled liquid causes a slowing down of the relaxation motions of the molecules which is responsible for the so called α-relaxation [3]. Decay of relaxation response function is usually described by the stretched exponential formula: $\Phi(t) = \exp(-t/\tau)^{\beta}$ proposed by Kohlrausch, Williams and Watts (KWW) [4] what seems to be an universal feature for all molecular glass formers. Temperature dependence of the relaxation time τ characterizing reorientational/diffusional movement of molecules in undercooled liquid differs from the Arrhenius law. It can be described by the formula: $\tau(T) = A \exp[B/(T-T_o)]$, based on the free-volume model proposed by Vogel, Fulcher and Tammann (VFT) [5], where A and B are material constants. On temperature approaching T_0 the cooperativity of motions increases drastically and the relaxation time τ diverges. The deviation of $\tau(T)$ from the Arrhenius behavior was used by Angell [6] to define the fragility parameter m for classification of glasses as the slope of the $\log[\tau(T)]$ vs. T_g/T curve at $T = T_g$, namely: $m = d(\log\tau(T))/d(T_g/T)$. From the microscopic point of view below T_g the system is quenched in one of the metastable states with molecules localized in a complicated arrangement of the potential energy barriers [7]. The molecules are unable to move towards more energetically favorable positions in time scale shorter than 100 s [3]. In relaxation spectroscopy the temperature at which relaxation time reaches this value is commonly accepted as the glass transition temperature T_g. On the other hand there are still present much faster small angle reorientational and conformational motions of the molecules, which could be detected through the observations of two kinds of the β-relaxation characterized by relaxation times of the order of 10^{-5} s [8] and 10^{-11}s [9], respectively.

The dielectric relaxation spectroscopy is an important tool for investigations of the dynamic behavior of the dipolar molecules of liquid and liquid crystalline glass former in the wide frequency range (10^9 - 10^{-1} Hz) available in the experiment [10]. This scale can be further widened up to hours through real time observations by an adiabatic calorimetry [11], which “belongs to time-domain spectroscopy corresponding to the frequency range between 10 mHz and 1 μHz”.

The aim of the paper is to show and discuss the results of the enthalpy relaxation for isopentylcyanobiphenyl (5*CB) in comparison to the earlier results of the dielectric relaxation spectroscopy [12].

The data concerning the polymorphism of the 5*CB sample obtained in the adiabatic calorimeter experiments are also presented as containing new information in respect to that reported earlier in our dielectric, DSC and polarizing microscopy studies [13,14].

EXPERIMENTAL

The sample of the right-handed isopentylcyanobiphenyl was synthesized at Organic Chemistry Laboratory of Military University of Technology in Warsaw. Heat capacity measurements of the sample were carried out by automated adiabatic calorimeter over the temperature range 100 - 300 K. The quantity of the sample loaded in the calorimeter cell was 8.718 g (0.034825 mole). Helium gas at normal pressure was charged into the dead space above the level of the sample (which is liquid at room temperature) to enhance the thermal equilibrium between the sample and the cell.

The heat capacities of the sample in liquid, cholesteric, glassy and crystalline states and for the empty calorimeter cell were determined in "normal" (point after point) mode in several runs on heating under adiabatic conditions. Additionally the scanning runs at constant heat flow both on heating and cooling, depending on the sign of the temperature difference between the adiabatic shield and calorimeter cell were also performed for detection of the phase transitions. Special thermal treatment, i.e. cooling and/or heating with different rates and annealing, were used for growing the crystalline phases of the substance. Independent enthalpy runs for determination of the thermodynamic parameters of the phase transitions were also performed.

Dielectric permittivity $\varepsilon(\nu, T) = \varepsilon'(\nu, T) - i\ \varepsilon''(\nu, T)$ has been measured in the temperature range from 300 K to 200 K with the Novocontrol spectrometer in the frequency range from 10^{-1} Hz to 10^5 Hz as was described previously [12].

POLYMORPHISM

Molar heat capacities of the glassy state, cholesteric phase and isotropic liquid (open circles) and two crystalline phases (filled circles) of the sample under study are plotted in Figure 1. The glass of the cholesteric phase was obtained easily by cooling of the cholesteric phase even with a very slow cooling rate. The glass transition anomaly occurred at the temperature T_g = 210.5 K ± 0.3 K established as the middle point between tangents to specific heat curves above and below. It was practically independent of the cooling rate used previously (usually rather slow). The heat capacity data of the undercooled liquid are missing between ca. 240 and 264 K because of the crystallization taking place in this temperature range.

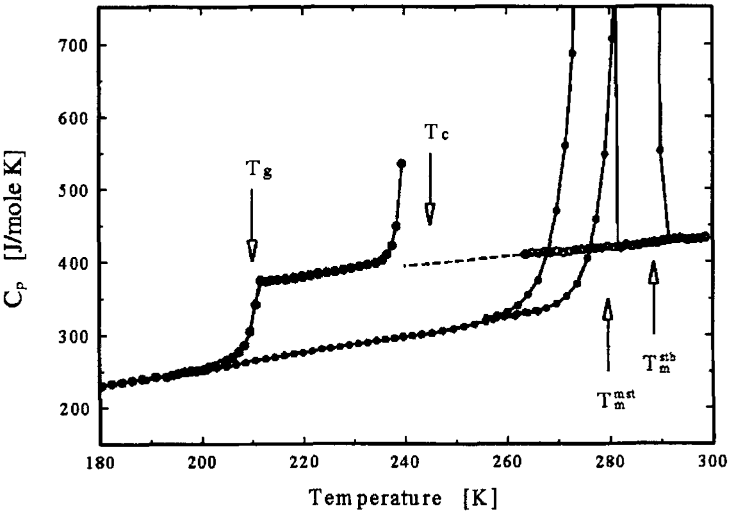

FIGURE 1 Molar heat capacities of 5*CB (chosen runs only) for glass, cholesteric phase and isotropic liquid (also undercooled) – open circles and metastable and stable crystals – filled circles.

In DSC measurements reported in [13] the crystallization occurred just above cholesteric phase – isotropic liquid phase transition only after special thermal treatment including the cooling below glass transition and further annealing for a few hours at about 230 K. That was explained by the idea that nucleation of the metastable crystal has a highest driving force below transition from isotropic liquid to cholesteric phase on

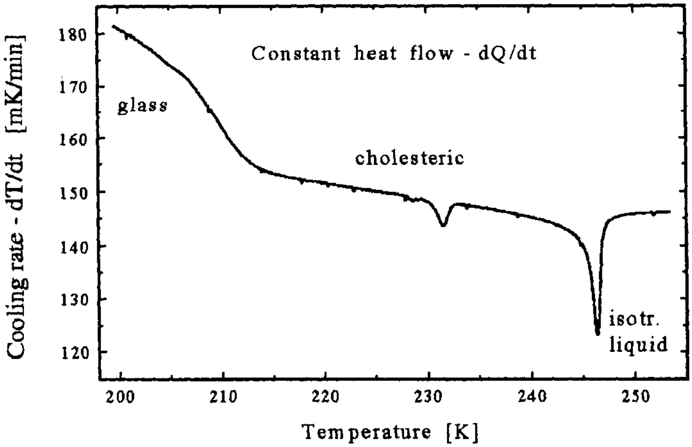

FIGURE 2 Cooling rate *dT/dt* during cooling the sample with constant heat flow.

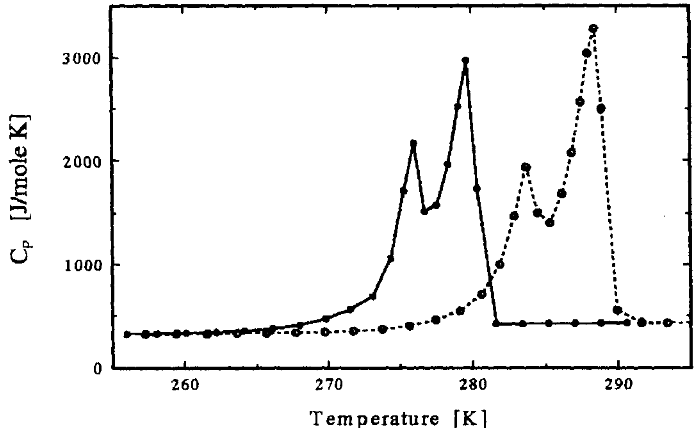

FIGURE 3 Molar heat capacities of 5*CB in a vicinity of melting for metastable (solid line) and stable crystals (dashed line).

cooling. That is now evidenced experimentally. In Figure 2 (compare with Fig. 2 in [13]) the drift of the temperature *dT/dt* vs. *T* observed on cooling the sample with a constant heat flow shows a small anomaly at ca. 230 K connected, as we suppose, with the nucleation process occurring in the cholesteric phase. Moreover, in DSC experiment for a very small sample (amounting to less than ca. 20 mg of the substance) the process of the crystallization was not detected even during long-lasting observations, whereas for larger samples it was very slow. So it looks like the crystallization takes place only in the bulk material. The fact that the transformation to the metastable crystalline phase occurred in adiabatic calorimeter for a big sample quite easily supports this statement.

The sample can be also transformed to the stable crystalline phase. The transformation takes place by partially melting of the metastable crystal and needs relatively long time. The mixture of both crystalline phases obtained in such a way can be saved (by cooling) for a very long period so it behaves like an experimentally stable state. On further heating the phases melt successively at the temperatures with a difference of almost 10 K between them. It was observed that the magnitudes of the specific heat anomalies due to the melting depend on the relative content of both crystalline phases in the initial mixture. The pure stable crystal was grown from such mixture by heating above melting point of the metastable phase followed by slow cooling down of the sample.

Large double heat capacity peaks due to melting occurred for both crystalline phases with maxima at 279.6 and 288.5 K for metastable and stable form respectively – Figure 3. Double peaks seem to be caused by a small contamination of the left-handed molecules in the sample of right-handed material. The enthalpy of melting of metastable and stable crystals ΔH_m^{mst} = 9.66 kJ/mol and ΔH_m^{stb} = 13.2 kJ/mol were determined by the standard method of adiabatic calorimetry. The thermodynamic parameters for cholesteric phase – isotropic liquid phase transition were not determined due to the spontaneous crystallization occurring in this temperature range, as mentioned above.

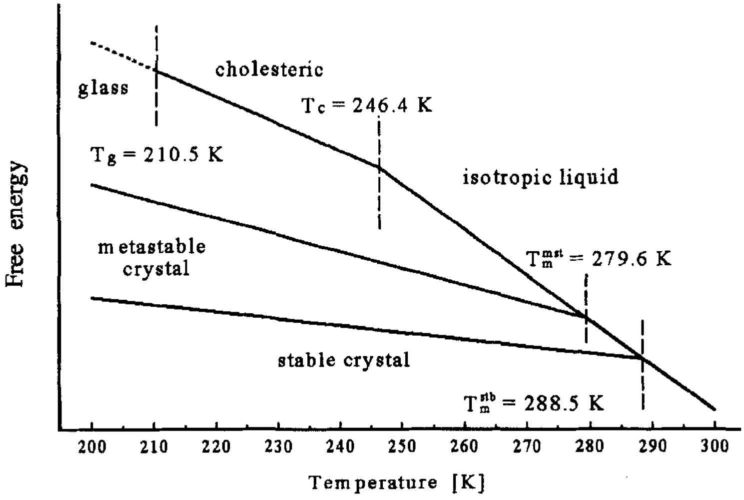

FIGURE 4 Schematic phase diagram for 5*CB.

Figure 4 presents the modified (in comparison to recently reported in [13]) schematic phase diagram for substance under study. All new details known from the present specific heat measurements are included. The isotropic liquid – cholesteric phase – glassy state form the enantiotropic system but together with both crystalline phases they form a monotropic system.

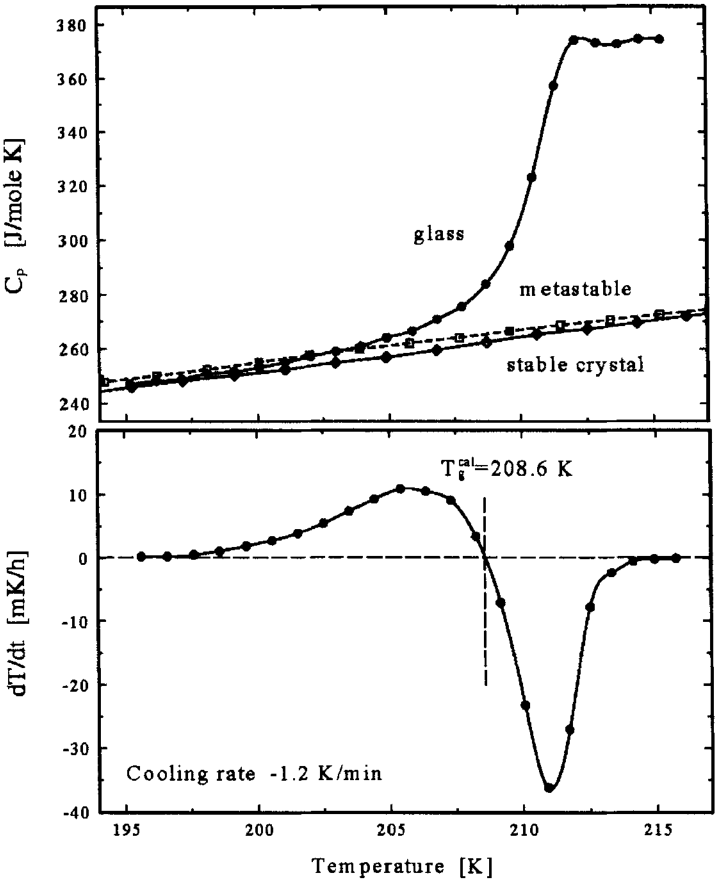

FIGURE 5 The spontaneous temperature drift rates due to enthalpy relaxation observed around T_g (bottom) and the heat capacities in an enlarged scale for the same temperature range (top).

RELAXATION

The contribution to the specific heat comes from both fast degrees of freedom (like internal vibrations) and usually much slower configurational ones (e.g. relaxational motions). In temperature approaching transition from liquid to glass the latter cannot keep pace with the rate of temperature changes applied on cooling the sample due to their slowing down. They undergo freezing in the state corresponding to some temperature close to T_g. This manifests itself as characteristic changes of the slope of the cooling curve seen well at the left side of Figure 2. From the thermodynamic point of view a glass is not an equilibrium state what enforces the relaxation of the system towards equilibrium state. Due to high thermal stability and temperature resolution of the calorimeter just such relaxation processes can be detected as a slow evolution of the temperature of the sample kept under adiabatic conditions. For the temperature range below T_g the glass has some excess configurational enthalpy H^{ex} in respect to equilibrium state and the enthalpy relaxation leads to the spontaneous self-heating process ($dT/dt > 0$). The evolution of the sample temperature can be described as an exponential growth. Fast heating of the sample in glass state up to some temperature above T_g leads to the state with a deficit of the configurational enthalpy (negative value of the H^{ex}) and consequently to self-cooling ($dT/dt < 0$), observed as an exponential decay of the sample temperature.

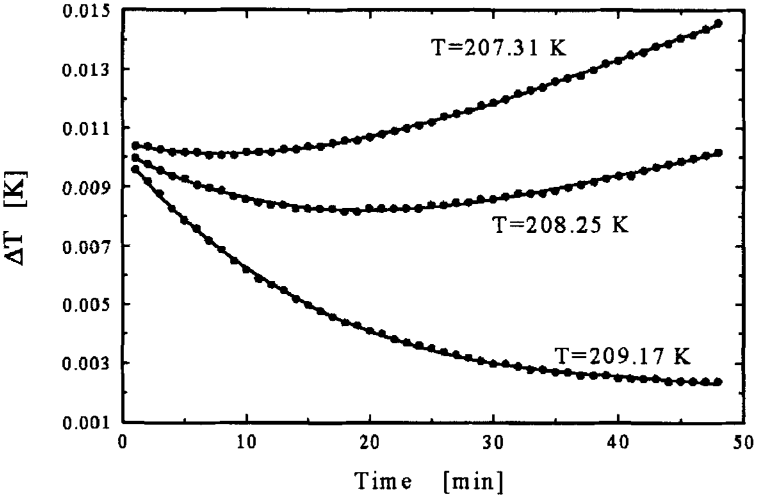

FIGURE 6 The spontaneous drifts of the sample temperature observed just below T_g^{cal} (two upper curves) and above T_g^{cal} (the lowest curve). Zero of the time scale corresponds to the 6th minute from the end of the heating period.

Figure 5 shows the rates of the temperature drifts dT/dt (bottom) registered 30 minutes after each of several heat inputs applied during standard heat capacity (top - filled circles) measurements for the sample cooled previously below T_g with the rate of ca. 1.2 K/min. The temperature where the rate dT/dt changes sign is a well-defined value usually called calorimetric glass transition temperature T_g^{cal}. Relatively large part of the curve corresponding to the self-cooling and low value of T_g^{cal} (in respect to T_g from specific heat data) mean that we have to do with a rather well annealed glass (in contrary to quenched one that was not able to grow due to limited cooling rate of our calorimeter). It should be stressed that for substance under study enthalpy relaxation process is evidently more complex than described above. It shows two components, namely below T_g^{cal} relatively fast self-cooling seen well (upper two curves on Figure 6) at the beginning of the equilibration period and much slower self-heating. Above T_g^{cal} both processes manifest themselves as self-cooling. Observed evolutions of the sample temperature for self-cooling processes both below and above T_g^{cal} were quite well fitted with a simple exponential function. They are connected with two different relaxation processes. First one is characterized by the relaxation time, which occurred practically independent of the temperature (in glass state $\tau \approx 2.5$ ks) as it is shown in Figure 8 (filled circles). For the second relaxation process which above T_g^{cal} manifests itself as self-cooling the corresponding self-heating process below T_g^{cal} occurred to be so slow that the observation time used in the experiment was too short for even rough estimation of its relaxation time.

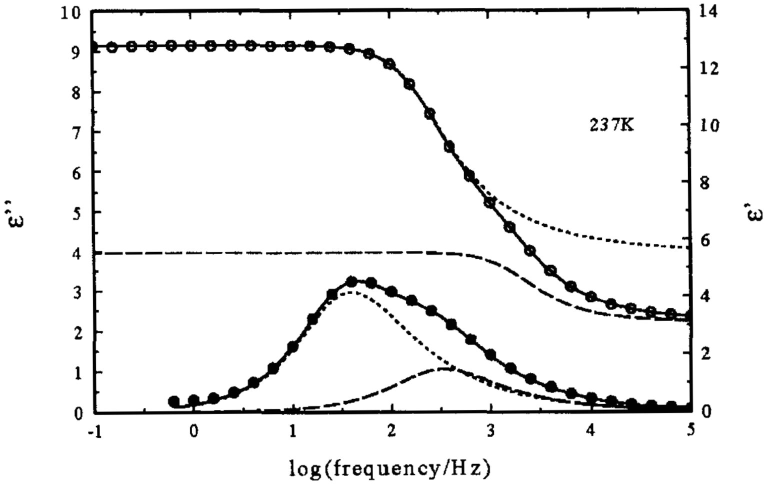

FIGURE 7 Relaxational changes of real electric permittivity ε' (open circles) and of dielectric loss ε'' (filled circles) vs. log ν observed at 237 K on cooling the cholesteric phase of 5*CB.

The same two relaxation processes were observed by means of dielectric spectroscopy. The observed spectra have been separated into two Debye type components shown for a chosen temperature in Figure 7. The main contribution is related to reorientation of the strong CN dipoles around the short molecular axes [12]. The smaller one can probably be explained by precession of the elongated 5*CB molecules around a director because it is absent in the isotropic phase [15]. Since the processes occurred in the same time scale it is natural that both of them are involved in the enthalpy relaxation. The effective dielectric relaxation times were compared with calorimetric results. The temperature dependence of both calorimetric and dielectric relaxation times for liquid phases occurred to be of non-Arrhenious type - Figure 8. The data obey the VFT equation with parameters: $T_0 = 178.3$ K, $A = 2\cdot10^{-12}$ s and $B = 490$ K obtained by fitting to the dielectric results [12,16]. It should be stressed that calorimetric relaxation times for cholesteric phase (open circles) lay quite well on the straight line describing the dielectric data. This fact indicates that above T_g both experimental methods observe the same microscopic mechanism of the relaxation. Thus during the transformation of the cholesteric phase to glass state the reorientation of the molecules around their short axes is being frozen.

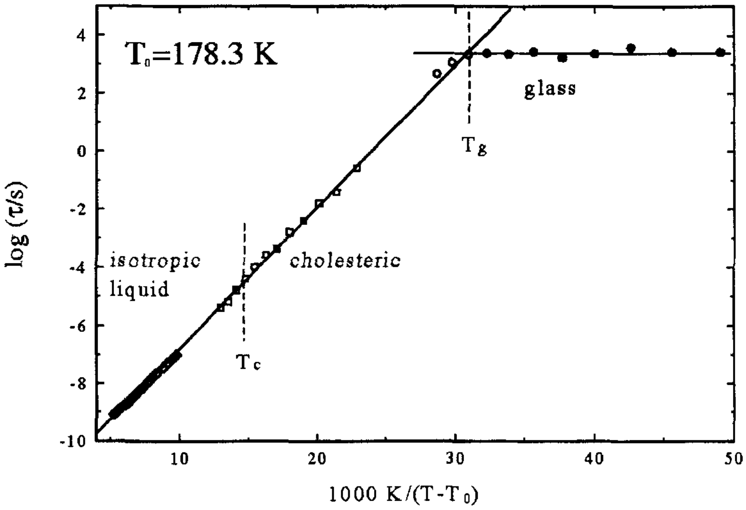

Fig.8. The relaxation times observed in the dielectric relaxation spectroscopy (open diamonds - [16], open squares - [12]) and in adiabatic calorimetry (open circles - cholesteric phase and filled circles - glass). Straight line fitted to dielectric data only.

Acknowledgments

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References

[1] Sidney R. Nagel, *Europhys. News* March/April 1998; R.J. Speedy, *J. Phys. Chem. B* **103**, 4060 (1999).

[2] J. Jäckle, *Rep. Prog. Phys.* **49**, 171 (1986).

[3] Sidney R. Nagel, *Phase Transitions and Relaxation in Systems with Competing Energy Scales*, ed. T. Riste and D. Sherrington, Kluwer Academic Publishers, Dordrecht, Boston, London 1993, p. 259.

[4] G. Williams and D.C. Watts, *Trans Faraday Soc.* **66**, 4019 (1984); M.R. de la Fuente, M. Perez Jumbindo and M.J. Tella, *Phys. Rev. B* **37**, 2094 (1988); A.K. Rajagopal and E. Wiegel, *Physica* **127A**, 218 (1984).

[5] H. Vogel, *Phys. Z.* **22**, 645 (1921); G.S. Fulcher, *J. Am. Ceram. Soc.* **8**, 339 (1923).

[6] R. Bohmer, K.L. Ngai, C. Angell and D.L. Plazek, *J. Chem. Phys.* **99**, 4201 (1993); M.L. Ferrer, H. Sakai, D. Kivelson and Ch. Alba-Simonesco, *J. Phys. Chem. B* **103**, 419 (1999).

[7] R.G. Palmer, D.I. Stein, E. Abrahams and P.W. Anderson, *Phys. Rev. Lett.* **53**, 958 (1984).

[8] G. Johari and J.W. Goodby, *J. Chem. Phys.* **77**, 5165 (1982); K.L. Ngai, *Phys. Rev. E* **57**, 7346 (1998).

[9] R. Zorn, A. Arbe, J. Calmenero, B. Frick, D. Richter and U. Buchenau, *Phys. Rev. E* **55**, 781 (1995).

[10] G. Williams, *J. Non-Crystalline Solids* **131–133**, 1 (1991); G.R. Brand, P. Lunkenheimer and A. Loidl, *Phys. Rev. B* **56**, R5713 (1997).

[11] H. Suga and S. Seki, *J. Non-Crystalline Solids* **16**, 171 (1974); H. Suga and S. Seki, *Faraday Discussions of Royal Soc. Chem.* **69**, 221 (1980).

[12] M. Massalska-Arodż, G. Williams, I. Smith, Ch. Connoly, G.A. Aldridge and R. Dąbrowski, *J. Chem. Soc. Faraday Trans.*, **94**, 387 (1998).

[13] J. Mayer, W. Witko, M. Massalska-Arodż, G. Williams and R. Dąbrowski, *Phase Transitions*, **69**, 199 (1999).

[14] W. Witko, J. Ściesiński, E. Ściesińska, M. Massalska-Arodż, J. Mayer and R. Dąbrowski, *Mol. Cryst. Liq. Cryst.* **330**, 391 (1999).

[15] M. Massalska-Arodż and J. Krawczyk, *SPIE* **4017**, 158 (1999).

[16] S. Urban, B. Gestblom and R. Dąbrowski, *Phys. Chem. Chem. Phys.* **1**, 4843 (1999).